VISCOSITIES TO 30,000 kg/cm²

BY P. W. BRIDGMAN

FURTHER ROUGH COMPRESSIONS TO 40,000 kg/cm², ESPECIALLY CERTAIN LIQUIDS

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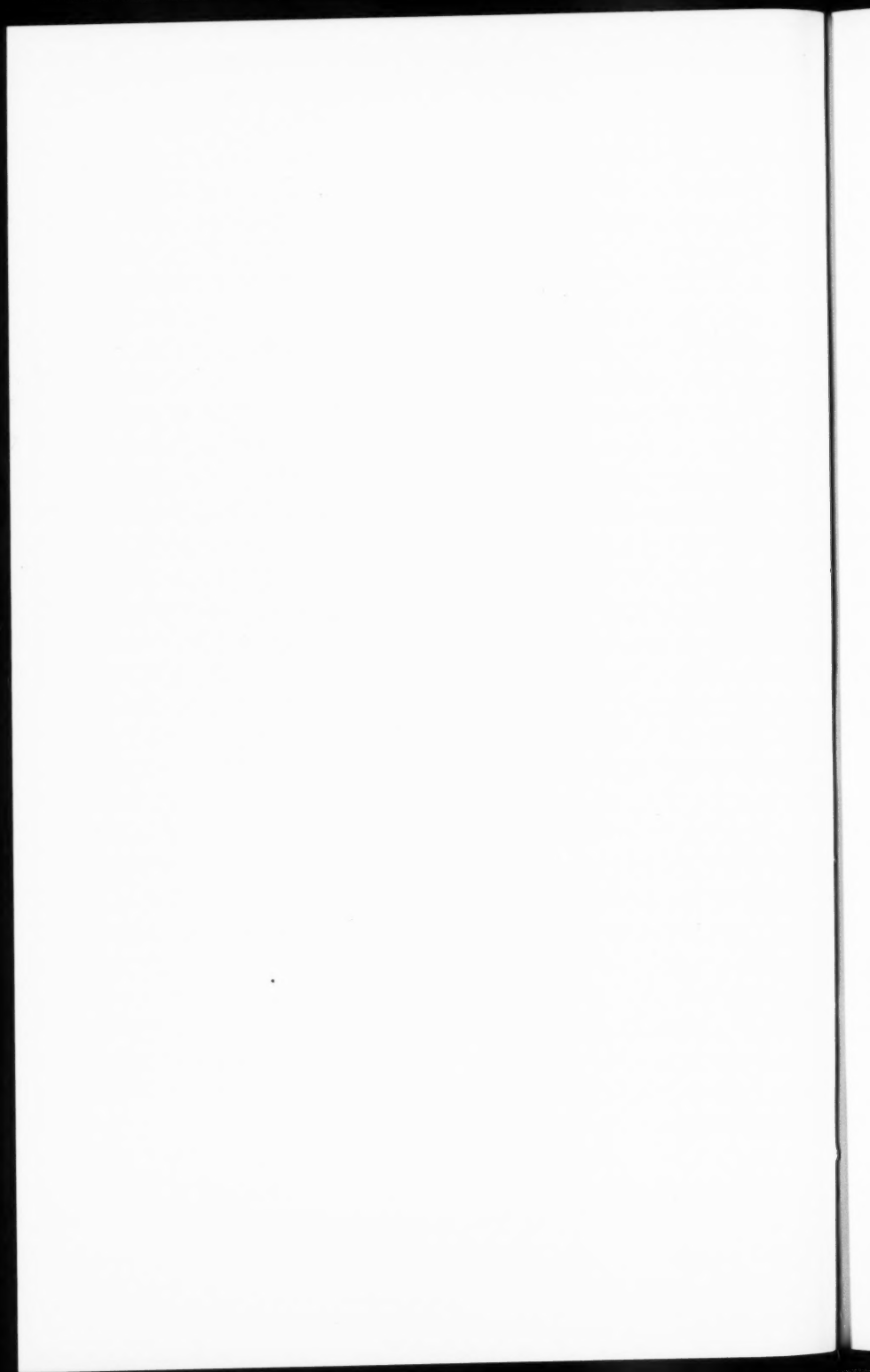
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By P. W. Bridgman

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INTRODUCTION

In a former paper[1] the viscosity of some 40 liquids was measured to 12,000 kg/cm². It was found that for most of these liquids viscosity increases to a first approximation exponentially with pressure—that is, the logarithm of the viscosity is a linear function of pressure. To a second approximation, for most of the liquids, the plot of logarithm of viscosity against pressure is at low pressures concave toward the pressure axis, but at higher pressures the curvature reverses, the curve becoming convex toward the pressure axis, and the viscosity increasing more rapidly than exponentially with pressure. The reversal of curvature usually occurs at a lower pressure for liquids with complicated molecular structure and with large absolute values of viscosity. For some of the simpler liquids formerly examined the reversal of curvature had not taken place below 12,000 kg/cm².

The techniques being now available for a considerable extension of pressure range,[2] the problem presents itself of extending former viscosity measurements to the widest possible range of pressure. There are at least two reasons for this. There is, in the first place, the purely practical matter of knowing what the viscosities at high pressures are of the liquids which have been used to transmit pressure. For example, in measuring compressibilities with the sliding wire method, effects were encountered a number of times which strongly suggested that the transmitting liquid was becoming so viscous under presssure as to interfere with the proper functioning of the apparatus immersed in it. How important this effect is can be answered by actual measurements of the viscosity of the transmitting liquid under pressure. In the second place, there is theoretical interest in finding whether the more rapid than exponential increase of viscosity found in the lower pressure range continues over the wider range.

The number of liquids available for measurement over the full range up to 30,000 kg/cm² is much restricted because of freezing induced by

pressure.   In the following, five pure liquids have been measured over the full range: methyl, n- and i-propyl, n-amyl alcohols, and i-butyl bromide.   These are nearly the only ones of the forty-three liquids of the former investigation available over the new range.   The propyl and amyl alcohols are beyond their freezing points under these conditions, but support the necessary subcooling without the formation of nuclei of the solid.   The first two even alcohols, on the other hand, ethyl and butyl alcohols, would not support supercooling without freezing under the conditions of these measurements, and could not be used.   Beside these five, the pressure transmitting liquid was also studied; this has been a mixture in various proportions of Eastman's "technical" i-pentane with "pentane."   In the light of these measurements it has become possible to improve somewhat the functioning of the transmitting liquid.

In addition to the measurements over the full pressure range on the liquids just enumerated, opportunity was taken to study the effect of pressure on a class of liquids not available at the time of the former measurements, namely various dimethyl siloxane polymers made by the Dow Corning Company, and also some of their commercial "Dow-Corning fluids."   Apart from the theoretical interest in these liquids, there is the practical question of whether they would not be suitable for pressure transmitting liquids.   They have already been used in this capacity at higher temperatures, above 200° C., for which they are especially adapted, but hitherto not at pressures above 5,000 kg/cm². The result of the present study is that the viscosity of these liquids, even the lowest members of the series, increases with abnormal rapidity with pressure, so that they are not suitable to replace pentane as a pressure transmitting medium in the ordinary range of temperature.

APPARATUS AND METHOD

The general scheme of the method is the same as before, namely a mechanical member falling under gravity through the liquid, the time of fall being determined by the breaking and making of an electrical contact.   The fact that now the high pressure container has to be in a single piece, however, demands essential geometrical modifications in the arrangements.   As before, the pressure apparatus is mounted on an axis, so that it can be rotated back and forth through 180°.   The axis of rotation is the longitudinal axis of hydraulic presses and high pressure vessel.   During rotation the hand pumps by which pressure is generated are disconnected, pressure being maintained by closing appropriate valves.   The falling member, instead of being a cylindrical weight falling vertically in a concentric cylinder, is now a vane or a bar, pivoted about an offset longitudinal axis, as indicated in Fig. 1.
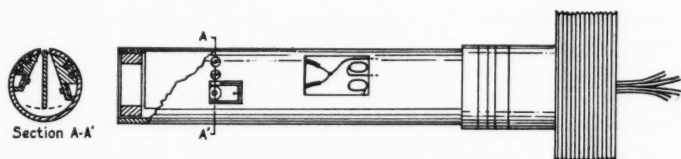
Section A-A'

FIGURE 1.   The swinging vane apparatus for measuring viscosity.

The vane rotated between stops, which were insulated and served at the same time to provide the electrical contact.   The angle of rotation between stops was about 60°.   The width of the vane was 1.0 cm. and its length 2.5 cm.   By varying the thickness of the vane the fall time may be varied and adapted to the viscosity of the liquid.   In this work two vanes were used—one of steel 0.003 inch thick, and the other of steel 0.030 inch thick.   The time of fall of the latter was about eight times that of the former.   This ratio was not enough to cover the whole range of viscosities.   For the highest pressures and the most viscous liquids the heavy vane was replaced by a bar of gold, 3 mm. in diameter and 2.5 cm. long, attached to the axis by two light arms, approximately 8 mm. long.   The fall of the gold bar was about forty-five times more rapid than that of the 0.030 vane.   The observed fall times varied from a minimum of about 2 seconds, below which the natural frequency of the timing apparatus introduced too large errors, to a maximum of about 6,000 seconds.   The total range of viscosity observed in the pressure apparatus was therefore 8 x 45 x 3000, or approximately one million fold.

Making and breaking of contact was indicated by the swing of the needle of a conventional portable voltmeter of about one second period connected in series with a B battery of 22.5 or 45 volts.   Timing was with a stop watch by observing the swing of the needle of the voltmeter.   The axis of the vane was positively grounded through a 0.001 copper wire, so that the contacts were definite and all metallic.   This constituted a distinct advantage over the contact arrangements of the falling weight of the former experiments in which part of the circuit might be through the thin layer of liquid at the lug of the falling weight.

For most of the liquids even the thinnest vane, 0.003 inches, gave too short fall times at atmospheric pressure.   Connection was made with the atmospheric viscosity by an auxiliary apparatus.   This consisted of a length of precision bore pyrex tubing from the Fish-Schurman Corporation.   The internal diameter was about 0.25 inch, and the length about 15 inches.   This was mounted vertically in a temperature bath, and filled with the liquid in question.   Relative vis-

cosities were obtained by timing the fall in the tube of a cylindrical aluminum weight with hemispherical ends. The weight was kept concentric, so that the fall was without yawing, by three small lugs at top and bottom. Observation of the fall time was made at 20° and 25° so as to provide the data for temperature correction to the pressure runs, which were made at room temperature, usually between 23° and 24°. Relative viscosities were converted to absolute viscosities by observing the time of fall in distilled water. Connection was made between the times in the atmospheric apparatus and the pressure apparatus by observing the time in both pieces of apparatus with a liquid viscous enough to give a long enough time for accuracy in the vane apparatus. This liquid was a heavy lubricating oil. The vane apparatus and the falling weight apparatus at atmospheric pressure differed by a further factor of about 500 in the equivalent fall times, so that altogether viscosities were measured over an extreme range of 5×10^8. This is much greater than the extreme range of observed viscosities of the former work, which was about 1,000 fold. It is true that in the former paper a pressure effect of 10^7 was mentioned (for eugenol), but this was by an extrapolation.

The entire pressure apparatus was filled with the liquid to be measured. It would have been too complicated in the small dimensions available to attempt to separate the transmitting liquid from the liquid to be measured, as was done formerly. The manganin gauge for measuring pressure was therefore also immersed in the same liquid, and this further demanded that the liquid be a sufficiently good electrical insulator. This procedure would not have been possible formerly with some of the alcohols, which were conductive enough to disturb the readings of the manganin coil. However, this effect fortunately did not prove troublesome at the higher pressures used here—the "water kick" in the reading of the coil almost entirely disappearing at pressures above 10,000 kg/cm^2.

Different set-ups with different vanes had to be made for different pressure ranges with the same liquid. Thus with i-propyl alcohol the range from 5,000 to 15,000 kg/cm^2. was covered with the 0.003 inch vane, the range from 15,000 to 25,000 with the 0.030 inch vane, and the range from 18,000 to 29,000 with the gold bar. The logarithms of the fall times were plotted against pressure, with the addition of an appropriate constant for each range so that the observed points overlapped smoothly from one range to the next. When the additive constant was determined in this way, it also resulted that all the points for the three ranges lay on a single smooth curve, thus affording evidence of the consistency of the measurements. The logarithmic constant in the lowest range was so determined as to piece on smoothly

with the former measurements in the range up to 12,000.   This again
was always possible.   In the illustrative example of i-propyl alcohol,
shown in Figure 2, there are checking measurements in the range be-
tween 5,000 and 12,000 for the two sets of measurements, by different
methods and separated by 23 years in time.   The slightly divergent
point near 5000 was because the fall time (with the vane) was too
short.   The check was in all cases most gratifying; the order of the
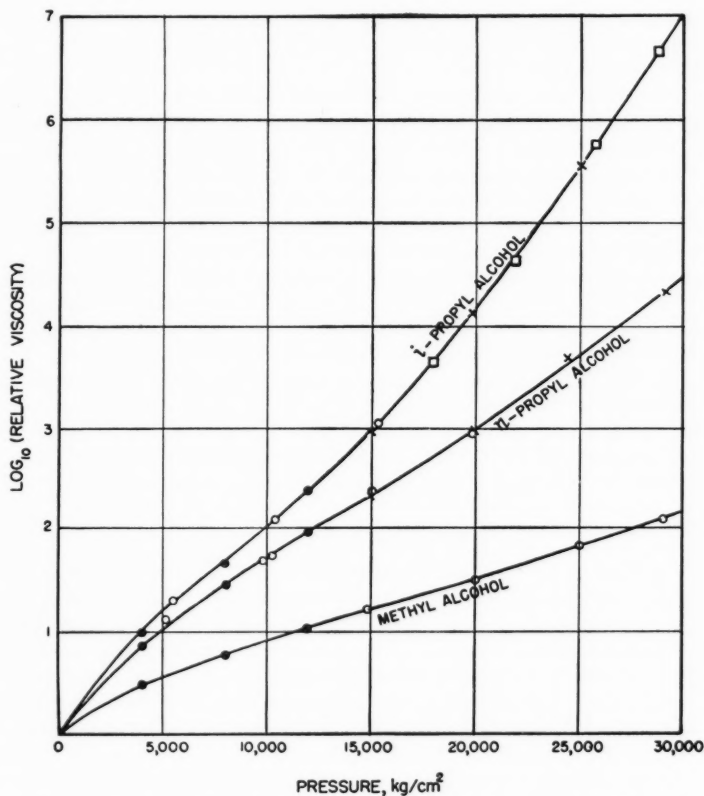agreement is indicated in Figures 2 and 3.

FIGURE 2.   Logarithm of relative viscosity of methyl, n-propyl and i-propyl
alcohols as a function of pressure (room temperature).   See text for the
symbols.

The observed fall times are proportional to the viscosity except for two correction terms—one depending on the buoyancy of the liquid, and the other on the change of linear dimensions of the apparatus produced by hydrostatic pressure. A simple dimensional analysis shows that viscosity is proportional to time multiplied by the linear dimensions of the apparatus multiplied by the difference of density of the vane and the liquid. Since the compressibility of both steel and the liquids is known, the correction factors may be determined. At 30,000 the additive correction on the logarithm of the fall time varies from a minimum of -0.018 for the lighter liquids, to -0.040 for ethyl bromide. On a total logarithm varying from 5 to 6 this correction is almost negligible.

Of the liquids measured in the following, all except the siloxanes were regular Eastman chemicals, used without attempt at further purification. The n-amyl alcohol was designated as "practical." The dimethyl siloxane polymers and the Dow Corning fluids I owe to the courtesy of Mr. Shailer L. Bass of the Dow Corning Corporation. The pure individuals were specially prepared by fractional distillation, of which those embracing 2 to 8 silicons in the chain were furnished. Of these the trimer, $Si_3O_2(CH_3)_8$, tetramer, $Si_4O_3(CH_3)_{10}$ hexamer, $Si_6O_5(CH_3)_{14}$, and octamer, $Si_8O_7(CH_3)_{18}$, were measured for viscosity. The compressibility of all of them has also been measured.[3] The first of the series, the dimer, was not measured for viscosity because it freezes at a low pressure. It was a surprise that none of the higher members of the series were brought to freeze at any pressure, either by pressures up to 12,000 in the present viscosity measurements, or by pressures up to 40,000 in the compressibility measurements. The reason for this should be investigated further.

THE EXPERIMENTAL RESULTS

In Figures 2, 3, 4, and 5 the experimental results are shown graphically, with the individual points. In these figures the logarithm to the base ten of the relative viscosity, corrected as described, is plotted against pressure in kg/cm². The points obtained with different set-ups are differently designated; those with the 0.003 inch vane by an open circle, those with the 0.030 inch vane by a cross, and those with the gold bar by a square. Solid circles show points on the curves obtained in the previous measurements up to 12,000. Smooth curves were drawn through the experimental points, and the numerical values at regular pressure intervals read off and tabulated in Tables I to III.

In Figure 2, the results are shown for methyl, n-, and i-propyl alcohols, and in Figure 3 for n-amyl alcohol, n-butyl bromide, and

i-pentane. The numerical results are collected in Table I. In all cases logarithm of viscosity against pressure turns upward at high pressures, although the upturn may be deferred to as much as 20,000 kg/cm² for methyl alcohol. The largest effect at 30,000 is shown by i-propyl alcohol, for which the viscosity has increased nearly 10⁷ fold (extrapolated from 29,000). Initially, however, the rate of rise for i-propyl alcohol is not as rapid as for n-amyl alcohol, the two curves crossing in the neighborhood of 20,000.
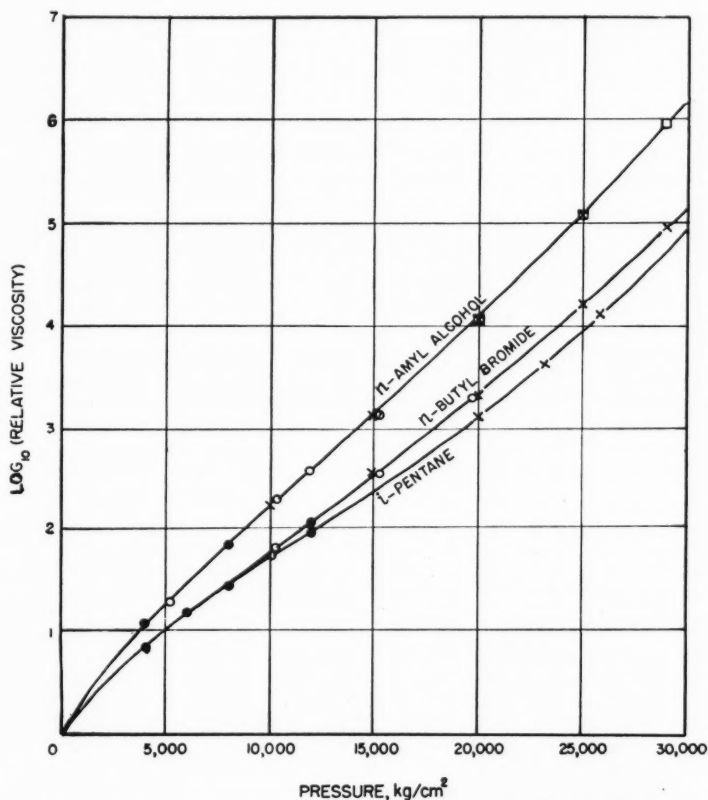

FIGURE 3. Logarithm of relative viscosity of n-amyl alcohol, i-pentane, and n-butyl bromide as a function of pressure. See text for the symbols.

TABLE I

Pressure kg/cm²	Log₁₀ (Relative Viscosity)					
	Methyl Alcohol	n-propyl Alcohol	i-propyl Alcohol	n-amyl Alcohol	n-butyl Bromide	i-pentane
0	0.000	0.000	0.000	0.000	0.000	0.000
5,000	0.650	1.014	1.168	1.290	1.004	1.026
10,000	0.890	1.684	1.990	2.224	1.722	1.720
15,000	1.200	2.328	2.960	3.150	2.548	2.342
20,000	1.482	2.966	4.116	4.096	3.326	3.122
25,000	1.810	3.708	5.490	5.100	4.228	3.980
30,000	2.152	4.500	6.986	6.192	5.146	4.930

TABLE II

VISCOSITY OF SEVERAL DIMETHYLSILOXANE POLYMERS

Pressure kg/cm²	Log₁₀ (Relative Viscosity)			
	Trimer	Tetramer	Hexamer	Octamer
0	0.00	0.00	0.00	0.00
2,000	0.86	0.94	0.98	1.01
4,000	1.50	1.63	1.73	1.83
6,000	2.13	2.40	2.66	2.87
8,000	2.94	3.53	4.05	4.52*
10,000	4.19	5.26	6.46	6.03
12,000	6.39	——	——	——

* at 9,000

TABLE III

VISCOSITY OF SEVERAL "DOW-CORNING FLUIDS"

Pressure kg/cm²	Log₁₀ (Relative Viscosity)			
	500–1.00	500–2.00	500–12.8	200–100
0	0.00	0.00	0.00	0.00
2,000	0.86	0.98	1.13	1.05
4,000	1.50	1.73	2.15	2.15(b)
6,000	2.13	2.63	3.57(a)	2.87(b)
8,000	2.95	3.91	4.66	——
10,000	4.26	——	——	——

(a) at 7,000   (b) at 5,000
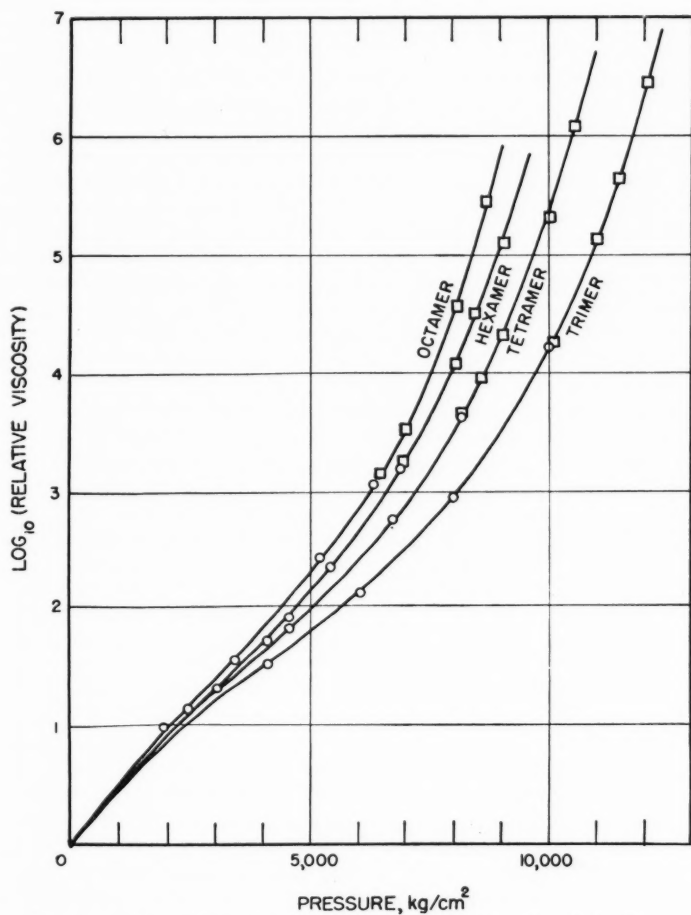
FIGURE 4. Logarithm of relative viscosity of four dimethyl siloxane polymers. See text for the symbols.

The results obtained with the mixtures of pentanes are not reproduced in detail here, since the material was not well enough defined to have scientific significance, nor were the measurements as complete over the full range. From the point of view of technique, however,
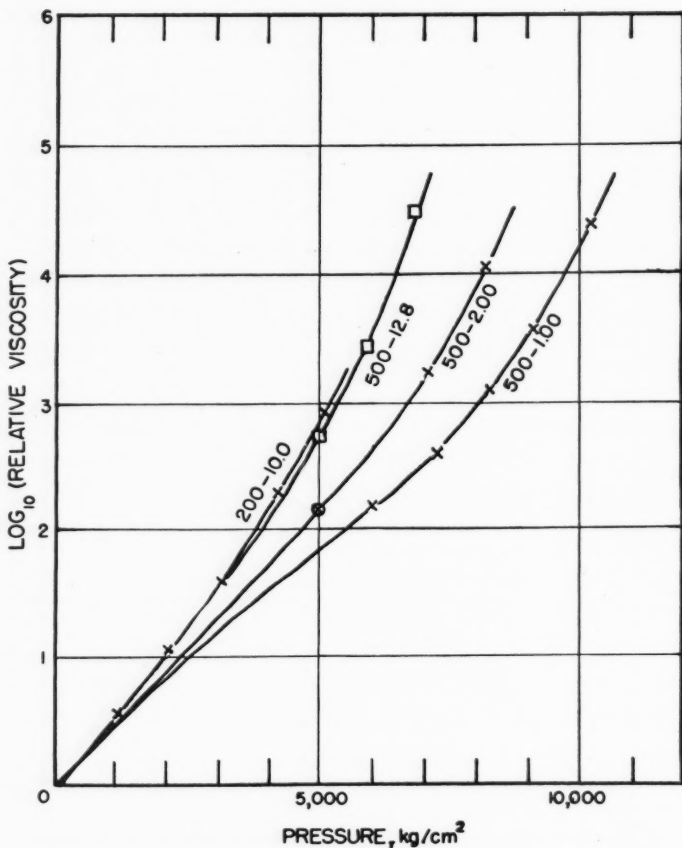
FIGURE 5. Logarithm of relative viscosity of several "Dow-Corning fluids." See text for symbols.

it is worth mentioning that a mixture of equal parts of Eastman's i-pentane and "pentane" ("technical") is at 30,000 less viscous than Eastman's i-pentane by a factor of 2, and pure "pentane" is less viscous than i-pentane by a factor of 3.5. Furthermore, the "pentane" did not freeze under these conditions at room temperature, so that it may well replace i-pentane or mixtures as the pressure transmitting

liquid. The absolute viscosity of i-pentane at 30,000 at room temperature is about 170 poises.

In Figure 4 and Table II the results are shown for four pure dimethyl siloxane polymers, the trimer through the octamer, and in Figure 5 and Table III for several "Dow Corning Fluids" of the 500 and 200 series, which are mixtures of the dimethyl siloxane polymers. The corrections for buoyancy and change of linear dimensions were so small for these liquids that they were not applied. The effect of pressure is so large on this class of substance that no attempt was made to carry the pressures above 12,000. Not only is the effect of pressure large, but the curvature is in all cases much greater than for any of the liquids of Table I, and the upturn begins at much lower pressures. This is all in accordance with results previously found, namely that the pressure effect and the curvature is greater for substances with more complicated molecules. This general trend is particularly well brought out in Figure 4 for the pure species. Another feature evident from the figures is that all members of the series have very approximately a common initial tangent at atmospheric pressure.

The very large pressure effect makes these liquids unsuitable for pressure transmitting media at high pressures, in spite of other desirable characteristics. Thus at atmospheric pressure the lowest member of the series which does not freeze under pressure, the trimer, is five times more viscous than i-pentane, whereas at 10,000 kg/cm² it has become 5,000 times more viscous.

Summary and Discussion

In this paper measurements of viscosity have been extended over a 2.5 fold increase of pressure range, from 12,000 to 30,000 kg/cm². The trends formerly found continue in the new range. Ultimately the viscosity increases with pressure more rapidly than exponentially. The pressure at which the upturn occurs is lower for liquids with more complicated molecules and the rate of upturn is more rapid.

The order of magnitude of the effect of pressure on viscosity is greater than that of any other known pressure effect, and would seem to indicate some essential difference in the mechanism. In viscous flow the molecules preserve their inviolability and must to a large extent function as individual wholes. In the case of long polymeric molecules, packed together like earth worms in a tin can, the phenomena of viscous flow must be quite different from those of specific heat or thermal expansion, for example, in which the parts of the molecules can function with a certain degree of independence. I have previously expressed this by saying that the pressure effect on viscosity involves an "interlocking" of the molecules. The accentuation of the effects

now found on increasing the pressure range seem to me to only accentuate the necessity for some such mechanism. It would seem to me that some essential physical modification is necessary in the pictures back of analyses such as those of Frisch, Eyring, and Kincaid,[4] for example, in which viscous motion is supposed to involve the passage of an activated complex from one equilibrium position over an intermediate potential hill to a new equilibrium position. Formally, it would probably be possible to include the new sort of thing by assuming, as they themselves indicate, that the activated complex itself is an aggregate of molecules, the degree of aggregation itself increasing rapidly with pressure. But physically it would seem that this is pretty close to the "interlocking" effect.

I am indebted to my mechanic, Mr. Charles Chase, for skillful construction and setting up of the apparatus.

LYMAN LABORATORY OF PHYSICS,
Harvard University, Cambridge, Mass.

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FURTHER ROUGH COMPRESSIONS TO 40,000 kg/cm², ESPECIALLY CERTAIN LIQUIDS

CONTENTS

Introduction and Technique

In this paper former rough measurements[1] of compression to 40,000 kg/cm² at room temperature of a number of solids are extended to substances initially liquid, the measurements in many cases being carried through the freezing point and on into the solid phase. This extension to the liquid phase has been made possible by a small change in technique, by which the liquid is sealed inside a lead capsule, and the overall compression of capsule with its contained liquid determined. A similar technique was formerly used in measurements to 50,000 over a temperature range,[2] but with a modification of detail. Formerly the lead capsule was sealed with a condenser discharge at the moment of impact of a lead plug pressed against the body of the capsule. With the present arrangement the walls of the capsule are so thin, the total thickness of the capsule being only 0.130 inch, as shown in Fig. 1, that the impact of the sealing plug would produce undue distortion and consequent mechanical extrusion of the liquid. Some less violent method of making the seal is therefore required. Ordinary soft soldering is ruled out for the same reason as before, namely too rapid heat transfer, with resulting thermal expansion and escape of the liquid.

The new technique employs essentially a cold soldering. The lead sealing point is lightly amalgamated with mercury, then lightly pressed against its seat in the capsule at the same time that it is rotated so as to spread the amalgamation to the seat, and finally held pressed against the seat with light pressure for 18 hours or more. By this time the mercury has diffused into the lead, leaving a solid solution, which is strong enough to withstand without leak the distortion of the capsule incident to carrying it to 40,000 and back, one or even several times. Lead is unique among all the soft metals whose binary mixture diagrams are given in Hansen[3] in the width of the range of composition in which the homogeneous solid solution is stable. Most soft metals
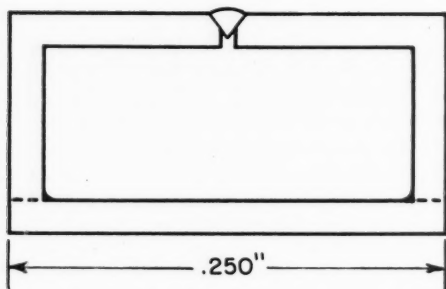
FIGURE 1. Scale drawing of the lead capsule for containing the liquid for measurements of compression. The seal is made by cold amalgamation under slight pressure of the conical plug.

break up into a liquid phase when amalgamated with mercury, so that the seal is not made. The cold amalgamation seal with lead was successful at once for nearly all the liquids tried. For some it was more difficult than for others, apparently the liquid itself forming some sort of surface film on the lead which was difficult to break through so as to obtain a contact sufficiently close for the solid sulution to grow across the surface. Several liquids were tried three or four times before success was attained, and there were one or two which were finally abandoned. Success was apparently easier to achieve if a slight amount of sodium was dissolved in the mercury, a practise long familiar in amalgamating copper for electrical contacts.

The methods of computation were simple extensions of those used before. The measured displacement of the piston has to be corrected for distortion of the carboloy piston and the compression of the lead sheath and of the steel washers. The total corrections were of the general order of 25% of the measured displacement. The initial volume of the liquid was calculated from its weight and density, the latter obtained either from the International Critical Tables or by special measurement in a specific gravity bottle.

It is characteristic of the compression of liquids that the initial increment of pressure is accompanied by a comparatively large volume change, the compressibility rapidly dropping at higher pressures. This means that the error from the friction exerted by the lead capsule is especially large at the low pressure end of the range. Furthermore, it is especially important to know the initial volume accurately, since this sets the fiducial mark from which all subsequent proportional changes of volume are calculated. The result was that it was neces-

sary to supplement the measurements in the 40,000 apparatus with
other measurements in an apparatus especially constructed for the
initial range from atmospheric pressure up to 5,000 kg/cm². The
primary function of this supplementary apparatus for 5,000 was the
same as that of the 40,000 apparatus, namely to permit rapid measure-
ments with moderate accuracy, so that it can be used as a tool for
exploration.

The supplementary apparatus is shown in Figure 2. The liquid
whose compression is to be measured is placed in the heavy steel cylin-
der A. Pressure is produced by advance of the piston, P, ½ inch in
diameter, and the volume change is given directly by the motion of the
piston measured by a dial gauge graduated to 0.001 inch and reading
by estimation to 0.0001 inch. This gauge is so connected to the cylin-
der and the mushroom plug as to minimize any distortion in the steel
parts and so as not to include at all any compression in the rubber
packing on the end of the piston, which operates on the unsupported
area principle. The compressing piston P is driven by a second piston
B, 2.0 inches in diameter, thus affording a sixteen fold multiplication
in pressure. The piston B is driven by a conventional hand pump,
connected through a dead weight piston gauge. The pressure is con-
trolled by the weight on the piston of the dead weight gauge, the weight
being adjusted and then the pump operated until the weight floats.
Readings were made at eleven different pressures between atmospheric
and 5,000, the spacing being nonuniform and closer at the lower end
of the range. Readings were made with increasing and decreasing
pressure, 20 in all, in order to eliminate error from friction. A special
feature of this apparatus, not used in any other of my pressure ap-
paratus, is the provision for rotating the pistons P and B before each
reading to minimize the effect of friction. To this end the packing on
the mushroom heads of both P and B is made unusually thin, only 1/64
inch thick on each. The packing material was usually neoprene, but
for some liquids which attack neoprene, such as xylene, varnished
cambric, such as is used in electrical insulation, was successfully used,
in three thicknesses, each .007 inch thick. The washers must obvi-
ously be cut with care, using a sharp cutter to obtain a smooth edge.
Use of such thin packing demands that the inner surfaces of the cylin-
ders in which P and B play be well polished.

Rotation was by hand, with a lever passing through a hole in the
piston B, back and forth through an angle of 60°. Usually three
double oscillations were made before each reading. It is not possible
with this apparatus, in contrast to the 40,000 apparatus, to make read-
ings as fast as the pressure manipulations can be made, but after every
increase of pressure an appreciable time must elapse for dissipation of
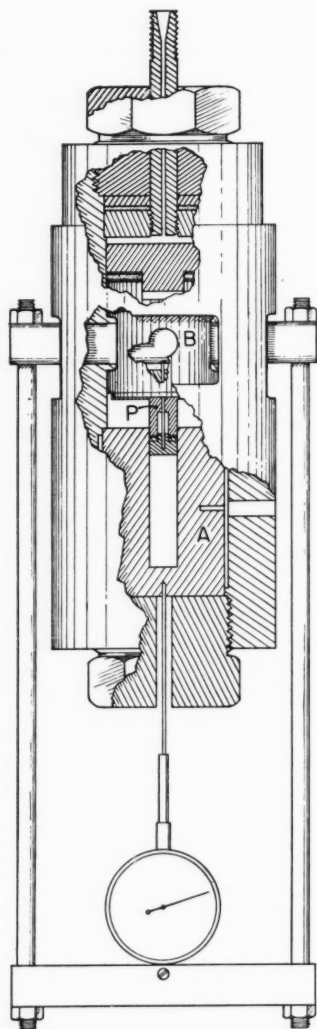
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FIGURE 2. The apparatus for rapid determination of the compression of liquids up to 5,000 kg/cm². Friction is minimized by rotation of the pistons P and B before the readings.

the heat of compression. The time may be decreased by placing in the body of the liquid several strips of sheet copper to conduct away the heat. In this way the time between readings was reduced to two minutes. The readings were taken on an exact time schedule to make the conditions as reproducible as possible. By taking all precautions, the difference between readings with increasing and decreasing pressure was practically never as much as 0.001 inch, and often materially less, on a total stroke of 0.5 inch. Friction should be reduced from the mean of readings as close together as this to a value smaller than that of the other errors.

The piston readings were converted to absolute compressions by means of blank runs with solids and liquids of known compressions in a way which need not be described in detail. The time required for a complete run was of the order of one hour, somewhat less than that required with the 40,000 apparatus. Operation so far has been confined to room temperature, which in the following may be taken as 25°, but there is no reason why temperature control and operation at other temperatures should not be added; in fact, a modified apparatus is now under construction for use at other temperatures. The time for a run will now naturally be increased by the time required for attainment of temperature equilibrium at each temperature.

The apparatus may be used for determinations of the thermodynamic freezing parameters of those liquids which freeze within the range by placing the liquid in an inverted steel cup with mercury seal, with water to transmit the pressure to the mercury, after the fashion of my early freezing curve determinations.[4] The apparatus was so used for a number of substances to be described in the following. By carrying the measurements beyond the freezing pressure up to 5,000, compressions of the solid phase are also obtained. The accuracy of these determinations is somewhat reduced as compared with that of the compressions of non-freezing liquids because of the reduced amount of liquid allowed by the presence of the water, mercury, and steel. In certain cases the freezing parameters had been previously determined in other apparatus better adapted to giving accurate values. In these cases the present data were adjusted to agree with the former results in the overlapping range, as will be described in detail later. There are also some cases in which compressions have been previously measured in the range from 5,000 to 50,000 kg/cm², but in which the low pressure range was not measured. The new data supplemented with the old now can allow complete values of compressions from atmospheric pressure to 40,000 kg/cm². The freezing temperatures and pressures given in the various tables have only an inferior accuracy, since the pressure steps were not made small enough to give good

values, the smallest being 200 kg/cm^2.   The differences of volume be-
tween liquid and solid are the differences at the temperature (25°) and
the pressure indicated, and should be fairly good for these conditions.
They are *not* the volume differences for the correct equilibrium pres-
sure at 25°, but differ from this by a term equal to the product of the
pressure excess (or defect) and the difference of compressibility be-
tween liquid and solid.

The Materials

The materials measured in the following include in the first place 30
hydrocarbons.   It was thought to be of interest to find whether the
compressions, particularly at the high pressure end of the range, tend
to assume any simple relation to the obvious properties of the molecule.
The 30 hydrocarbons selected include all those listed in Eastman's
catalogue of organic chemicals and procurable, including substances
both liquid and solid under ordinary conditions.   Most of these were
of the "Eastman" grade of purity; the n-dodecane, n-hexadecane, and
tetrahydronaphthalene were of "practical" grade, the amylene and
fluorene of "technical" grade, and the styrene was "stabilized with
tert.-butylcatechol."   Next comes a group of 8 miscellaneous organic
compounds.   The first six of these were from my own stock, left from
previous experiments, which seemed of interest for various reasons.
In addition there are two of the fluorocarbons developed during the
war, which I owe to the courtesy of Professor W. T. Miller of Cornell
University.   The first of these is perfluoroheptane, C_7F_{16}, prepared by
the vapor phase fluorination of heptane, utilizing the procedure of
Cady, Grosse, Barber, Binger, and Sheldon.[5]   It boiled at 82°.   The
second is a "chlorofluorocarbon polymer oil."   This was a fraction of
"stabilized" chlorotrifluoroethylene polymer of approximate boiling
range 100° to 200° at 0.3 mm, prepared as described by Miller, Ditt-
man, Ehrenfeld, and Prober.[6]   Finally there is a group of 16 sub-
stances which I owe to the courtesy of Mr. Shailer L. Bass of the Dow
Corning Co..   The first seven of these are the individual members of
the dimethylsiloxane polymers from the dimer through the octamer,
or in other words the compounds of the formula

$$(CH_3)_3SiO - \left[(CH_3)_2SiO \right]_x - Si(CH_3)_3$$
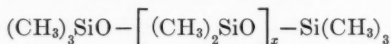
where x varies from 0 through 6.   The next eight are commercial
"Dow Corning" fluids of the 500 and 200 series of different viscosities.
The members of these two series are composed predominantly of
polymers of the type just described.   In the following these liquids
are identified in the regular manner by giving first the number of
the series and then the viscosity in centistokes.   Thus the liquid

designated as 500–2.00 is the liquid belonging to the 500 series with viscosity 2.00 centistokes.   Finally, there is a single member of the 550 series, which is a different type of compound than the others, in that a portion of the methyl groups are replaced by phenyl groups.

Comparison with Previous Measurements

The volume compression of liquid n-heptane has been previously measured[7] by the sylphon method at 0°, 50°, and 95° in the range of the liquid below 11,000 kg/cm^2.   Exact comparison with the present measurements is not easy because of the incompatibility of temperature range.   Linear interpolation of the previous results gives volume decrements at 500 and 5,000 kg/cm^2 of 0.0544 and 0.202 respectively against 0.0502 and 0.198 found now.   The difference is in the direction to be expected because of the inadequacy of a linear interpolation, and does not appear unreasonable in magnitude.

The volume compression of liquid n-octane was previously measured[8] in the same way as n-heptane in the same temperature range, but of necessity in a narrower pressure range because of the freezing. Linear interpolation as above gives for the volume decrements at 500 and 3,000 kg/cm^2 0.0444 and 0.149 respectively against 0.0444 and 0.146 found now.   The agreement at 500 is too good for the method of interpolation, and at 3,000 not unreasonable.

The volume compression of liquid n-decane[9] was determined under the same conditions as outlined in the two paragraphs above, the pressure range being correspondingly reduced.   The volume decrements at 500 and 1,000 kg/cm^2 by linear interpolation were 0.0417 and 0.0713 respectively against 0.0400 and 0.0683 found now.   The difference is in the right direction, but somewhat larger than appears a natural consequence of the method of interpolation.

Three previous sets of measurements have been made on benzene in the course of my high pressure work, not to mention work by other observers.[10]   The freezing parameters were determined with much care up to 12,000 kg/cm^2.   These values are doubtless better than those obtained with the present apparatus, and they were accordingly accepted and incorporated in Table II.   The fractional change of volume on freezing with the present apparatus was about 5 per cent lower than the value accepted from the previous work.   The volume compression of the liquid was measured in the former sylphon apparatus, but only at 50° and 95°.   The decrement at 24° and 680 kg/cm^2 (the freezing pressure at this temperature) was obtained by linear extrapolation from these two temperatures and is therefore rather uncertain.   Finally, the volume decrement of the solid phase from 5,000 as the zero has been determined.   The volume decrement

between 5,000 and 40,000 formerly found was 0.141, against 0.144 found now and given in Table II.   Exact comparison of these two results is not possible because the present results pertain to the low pressure modification of the solid, since no trace of the transition to a high pressure form was found which formerly occurred at 12,500 kg/cm². In the present work the transition was doubtless suppressed because of the small size of the apparatus and the low temperature, which was at the lower edge of the range in which the transition was previously observed.   The volume decrement at the transition formerly found was 0.008.   In comparing the previous results with the present for the low pressure modification the volume decrement is therefore to be taken as probably 0.149 at the maximum (assuming the two modifications to have the same compressibility), or somewhat less than 0.149 if the high pressure modification is assumed to be less compressible, as is probable.   In any event the agreement with the former high pressure values is not bad.

The freezing pressure of cyclohexane at 25° listed in Table II, 355 kg/cm², is taken from Deffet[11].   There is no doubt that his value is better than the mean value 420 kg/cm², given by the present work. It has already been explained that the pressure steps in the present work were so large that a minimum error of 100 kg/cm² in the equilibrium pressure is always possible.   The values above 5,000 given in the table are taken from my previous measurements[12] to 50,000. Measurements above 5,000 were not made with the present apparatus because cyclohexane was one of the liquids for which the sealing technique made so much difficulty that it was abandoned.   With regard to the previous work it is to be especially noted that the volume discontinuity at 7,500 listed there was incorrectly described as due to freezing; it is, as a matter of fact, due to a transition between two solid phases.

The freezing pressure of p-xylene is so low that the values of other observers were used for the low pressure end of the range.   The freezing pressure at 25° was taken as 343 kg/cm² from the work of Deffet,[13] and the fractional change of volume on freezing as 0.164 at the same pressure and temperature from the same author.   The compression of the liquid at 343 kg/cm² was assumed to be 0.0249 from the work of Richards and collaborators,[14] this being their value at 20°. There should be a small correction for the difference of temperature, but the data for this do not exist.   In connecting these low pressure values with the present measurements to 40,000 an extrapolation of the measurements on the solid of 1,000 kg/cm² was necessary.   Measurements have been previously made on the solid phase of this sub-

stance in the range above 5,000 kg/cm^2.   The volume decrement between 5,000 and 40,000 formerly found was 0.113 against 0.116 found now.

Methylene chloride (Table III) has been previously measured[15] above 5,000, so that the essentially new contribution of the present measurements is the compression of the liquid up to 5,000.   The former total volume decrement between 5,000 and 40,000 was 0.219 against 0.211 found now.   The agreement above 15,000 is perfect within the number of significant figures.   The former freezing parameters agree fairly well with the present ones.

The freezing parameters of chloroform have been previously measured[16] with considerable care; these former values are incorporated in Table III.   The compression has also been determined from 5,000 as zero up to 50,000.   The former value of the volume decrement between 5,000 and 40,000 was 0.204 against 0.203 found now.

Ethyl acetate has been previously measured[17] above 5,000.   In the former measurements data were obtained for both liquid and solid phases up to the maximum pressure; the natural tendency is for the liquid to subcool over the entire pressure range, so that special manipulation was necessary to obtain the solid phase.   With the present smaller apparatus and more rapid pressure variation the solid phase was not obtained at all.   The former volume decrement of the liquid phase between 5,000 and 40,000 was 0.185 against 0.178 found now.

The compression of the liquid phase of chlorobenzene has been previously measured[18] at 0°, 50° and 95° up to 11,000 kg/cm^2.   Reducing to 25° by linear extrapolation gives for the volume decrement at 5,000 and 25°, 0.1406 against 0.1517 found now.   The discrepancy is perhaps in the direction to be explained by the linear extrapolation, but is larger than usual and not obviously explainable.   Further, the volume decrements have been determined up to 50,000 from 5,000 as zero. The former volume decrement between 5,000 and 40,000 was 0.177 against 0.175 now.   The correct freezing pressure at 25° is probably nearer 5,000 than 7,500, the average figure given by this work.   It is to be marked that in the former work a second phase of the solid was encountered at pressures above 13,000 and at temperatures of 75° or more; no trace of this phase was found in the present work.

The compression of n-amyl ether has been measured[19] up to 50,000 from 5,000 as zero.   The total volume decrement between 5,000 and 40,000 was 0.197 against 0.187 found now.   The former freezing pressure given for 25° was 7,500, very materially lower than that now given, 11,140; neither of these values makes any pretense to accuracy.   The former volume decrement at the freezing pressure, 0.047, is much higher than that now given, 0.021, but is not inconsistent with it in

view of the difference of pressures, and indicates a compressibility for the liquid phase materially higher than that of the solid, as is normal.

THE RESULTS AND DISCUSSION

The results for the normal straight chain paraffins, containing 7, 8, 10, 12, 16, 18 and 28 carbons in the chain, are shown in Table I.   The

TABLE I

COMPRESSIONS OF NORMAL STRAIGHT CHAIN HYDROCARBONS

Pressure kg/cm²	$\Delta V/V_0$						
	n-hep-tane	n-oc-tane	n-dec-ane	n-dodec-ane	n-hexa-decane	n-octa-decane	n-octa-cosane
0	.0000	.0000	.0000	.0000	.0000 [e]	.0000	.0000
500	.0502	.0444	.0400	.0353	.1413		
1,000	.0835	.0751	.0683	.0609	.1576		
1,500	.1073	.0982	.0902	.0787 [d]	.1676		
2,000	.1266	.1170	.1079		.1756		
2,500	.1428	.1326	.1228	.1869	.1823	.0479	.0437
3,000	.1567	.1460	.1359		.1887		
3,500	.1688	.1579		[c]	.1951		
4,000	.1796	.1686			.2006		
4,500	.1893	.1782			.2056		
5,000	.1982	.1868 [b]	.2319	.2158	.2096	.0777	.0719
10,000	.2659 [a]	.2941	.2694	.2516	.2446	.1183	.1117
15,000	.3394	.3205	.2948	.2769	.2696	.1470	.1407
20,000	.3616	.3398	.3141	.2961	.2883	.1695	.1637
25,000	.3789	.3546	.3293	.3115	.3034	.1886	.1829
30,000	.3937	.3669	.3418	.3244	.3156	.2051	.1992
35,000	.4057	.3775	.3524	.3359	.3261	.2196	.2128
40,000	.4163	.3872	.3615	.3464	.3352	.2324	.2239

a Freezes at 11,450. $\Delta V/V_0$ .2782 and .3202
b Freezes at 5,510. $\Delta V/V_0$ .1863 and .2475
c Freezes at 3,050. $\Delta V/V_0$ .1370 and .2107
d Freezes at 1,700. $\Delta V/V_0$ .0839 and .1869
e Freezes at 420. $\Delta V/V_0$ .0300 and .1392 $\Delta V/V_0$ = .0192 at 250 and .1498 at 750

table exhibits definite regularities.   The first five of the series are liquid at atmospheric pressure at room temperature, and are brought to freeze by the application of pressure.   The pressure required for freezing decreases as the number of carbons in the chain increases.   A plot of the freezing pressure against number of carbons yields a smooth curve, rising very rapidly at the lower end.   The fractional disconti-nuities of volume on freezing are 0.0420, 0.0612, 0.0737, 0.1030, and 0.1092.   If these values are plotted against number of carbons a curve rising with increase of carbon number will be obtained, but the curve is not smooth.   A very considerable part of the rise with increasing carbon number is to be ascribed, not to an effect of structure, but to

the incidental effect of decreasing freezing pressure, since the volume discontinuity of nearly every substance increases as the freezing pressure is lowered. The initial compressibility in the liquid phase decreases as the number of carbons increases, as shown, for example, by the row of compressions for 500 kg/cm². This is in large part a reflecrion of the greater volatility of the lighter members of the series. The effect persists over the entire range, the compressions at 40,000 showing the same sequence. The initial effects reflecting the proximity of the critical point with the vapor might be expected to be wiped out at the upper end of the pressure range, where other sorts of structural effect might be expected to begin to become apparent. As a rough indication of this, the relative compression in the last 20,000 kg/cm² may be taken, that is the difference between the rows for 20,000 and for 40,000 kg/cm² in the table. The numerical values for the seven members of the series are respectively: 0.0547, 0.0474, 0.0474, 0.0503, 0.0469, 0.0629, and 0.0602. The tendency of the first five, for the paraffins initially liquid, is an irregular decrease with increasing carbon number. The last two, for those members initially solid, are on the average 25 per cent higher than the others. Part of this is to be ascribed to the fact that the initial V_0 on which the compressions are calculated is the volume of the solid rather than the larger initial volume of the liquid. However, not as much as half of the difference can be explained in this way, the difference of volume between solid and liquid at the atmospheric freezing point not being much over 10 per cent. Taking due account of this factor, there seems to be no outstanding regularity left in the compressions at the upper end of the pressure range. This means that other factors become more important than the simple size of the molecule.

In Table II are collected the compressions of the other 23 hydrocarbons. The arrangement is by number of carbons in the molecule. This means that substances initially liquid occupy the first part of the table and those initially solid the last part, with some overlapping toward the center. Obvious factors which might be taken into account in searching for correlations with the compressions are: the carbon-hydrogen ratio in the molecule, the ratio of the number of double bonds between carbons to single bonds between carbons and the type of molecular structure, whether straight chain, single ring, or double ring. Search has disclosed no obvious correlation between any of these factors and the initial compressibility, the total compression under 40,000 kg/cm², or the compression in the last 20,000 kg/cm². There are, however, certain gross regularities in the behavior of the hydrocarbons as a group. The total compression under 40,000 kg/cm² for those substances initially solid clusters around 0.2, ranging from a

TABLE II

COMPRESSION OF MISCELLANEOUS HYDROCARBONS

$\Delta V/V_0$

Pressure kg/cm²	Amylene	Benzene	Cyclo-hexane	Methyl Cyclo-hexane	Styrene	o-xylene	m-xylene	p-xylene	Cap-rylene	Cumene	Mesi-tylene
0	.0000	.0000	.0000 [b]	.0000	.0000	.0000	.0000	.0000 [h]	.0000 [i]	.0000 [j]	.0000
500	.0642	[a]	.0812	.0353	.0316	.0321	.0352		.0458	.0348	.0333
1,000	.1016		.1021	.0637	.0544	.0561	.0602		.0763	.0593	.0572
1,500	.1288		.1179	.0862	.0728	.0748	.0802		.0988	.0788	.0756
2,000	.1500		.1302	.1042	.0884	.0902	.0968		.1174	.0950	.0914
2,500	.1672	.1992	.1420	.1196	.1017	[f]	.1109	.2243	.1331	.1087	.1053
3,000	.1818		.1526	.1332	.1136 [e]		.1236		.1467	.1207	.1177 [k]
3,500	.1946		.1622	.1452			.1350		.1587	.1315	.1290 [k] }
4,000	.2060		.1719	.1558			.1452		.1691	.1413	.1629
4,500	.2162		.1809	.1655			.1543		.1782	.1503	
5,000	.2255	.2314	.1880	.1745	.1942	.2029	{ .1624 / .2117 [g] / .2211 }	.2503	.1867	.1586	.1817
10,000		.2731	.272 [c]	.2308 [d]	.2362	.2396	.2461	.2820	.2419	.2135	.2299
15,000		.3007	.298	.2663	.2638	.2643	.2721	.3054	.2779	.2488	.2615
20,000		.3217	.318	.2910	.2842	.2832	.2919	.3230	.3041	.2738	.2827
25,000		.3385	.334	.3106	.3002	.2992	.3077	.3370	.3241	.2928	.2990
30,000		.3526	.348	.3266	.3136	.3112	.3209	.3485	.3400	.3076	.3123
35,000		.3659	.359	.3401	.3253	.3212	.3323	.3582	.3532	.3196	.3240
40,000		.3758	.369	.3516	.3355	.3298	.3425	.3666	.3649	.3294	.3345

a Freezes at 680. $\Delta V/V_0$ .0634 and .1596

b Freezes at 355. $\Delta V/V_0$ .0326 and .0742. $(\Delta V/V_0)_{iq.} =$ .0233 at 250

c Transition at 7,500. $\Delta V/V_0$ 0.216 and 0.257

d See text

e Freezes at 3,120. $\Delta V/V_0$ .1162 and .1647

f Freezes at 2,300. $\Delta V/V_0$ .0983 and .1690

g Freezes in this region. Upper figures for liquid, lower for solid.

h Freezes at 343. $\Delta V/V_0$ .0249 and .1889

i Liquid throughout

j Liquid throughout

k Freezes at 3,500

TABLE II (*Continued*)

COMPRESSION OF MISCELLANEOUS HYDROCARBONS

$\Delta V/V_0$

Pressure kg/cm²	Naph-thalene	Tetra-hydro-naph-thalene	Dipen-tene	β-methyl naph-thalene	Ace-naph-thene	Di-phenyl	Fluor-ene	Anthra-cene	Di-benzyl	Fluor-anthene	Hexa-ethyl benzene	Tri-phenyl Me-thane
0	.0000[l]	.0000	.0000[n]	.0000[o]	.0000[o]	.0000[o]	.0000[o]	.0000[o]	.0000[o]	.0000[o]	.0000[o]	.0000[o]
500		.0249	.0339									
1,000		.0447	.0583									
1,500		.0608	.0773									
2,000		.0745	.0930									
2,500	.0364	.0866	.1066	.0483	.0338	.0429	.0373	.0305	.0457	.0373	.0361	.0354
3,000		.0974	.1187									
3,500		*m*	.1294									
4,000			.1389									
4,500			.1473									
5,000	.0636	.1763	.1549	.0780	.0568	.0705	.0615	.0539	.0772	.0615	.0617	.0601
10,000	.1021	.2106	.2085	.1190	.0899	.1086	.0974	.0876	.1219	.0974	.0984	.0956
15,000	.1295	.2359	.2434	.1483	.1149	.1361	.1247	.1132	.1521	.1247	.1254	.1225
20,000	.1513	.2546	.2669	.1713	.1346	.1574	.1464	.1336	.1747	.1464	.1465	.1444
25,000	.1698	.2695	.2832	.1905	.1507	.1753	.1649	.1509	.1929	.1649	.1645	.1627
30,000	.1858	.2822	.2966	.2067	.1648	.1905	.1803	.1657	.2086	.1803	{ .1809[p] / .1909 }	.1781
35,000	.1996	.2937	.3083	.2206	.1776	.2035	.1937	.1792	.2223	.1937	.2072	.1912
40,000	.2114	.3041	.3188	.2325	.1893	.2146	.2055	.1911	.2343	.2055		.2025

l Solid throughout
m Freezes at 3,050. $\Delta V/V_0$ .0984 and .1599
n Liquid throughout
o Solid throughout
p Sluggish transition here, not complete

minimum of 0.189 for acenaphthene to a maximum of 0.234 for di-benzyl.   The solid normal paraffins also fall within the same range. For hydrocarbons initially liquid, on the other hand, the total compression under 40,000 kg cm², including in this the volume change on freezing, ranges from a minimum of 0.304 for tetrahydronaphthalene to a maximum of 0.416 for n-heptane.   Included in this range are the three liquids which are not forced to freeze by the maximum pressure, namely caprylene, cumene and dipentene.   It is probable that the non-freezing of these liquids is a subcooling effect, accentuated by imperfect purity.   The fact that the compressions at 40,000 of those substances which remain liquid are not materially different from those which have passed from the liquid to the solid phase means that sufficiently high pressures force the liquid into approximately the same volume as the crystal lattice.   Or expressed differently, the volume of a glass is not greatly different from that of the corresponding crystal.

TABLE III

COMPRESSION OF MISCELLANEOUS NON-HYDROCARBONS

Pressure kg/cm²	$\Delta V/V_0$							
	Methylene chloride	Chloroform	Ethylene bromide	Ethyl acetate	Chlorobenzene	n-amyl ether	Fluorocarbons	
							light	oil
0	.0000	.0000	.0000	.0000d	.0000	.0000	.0000	.0000
500	.0400	.0404	.0267$_c$	.0446	.0311	.0401	.0703	.0275
1,000	.0683	.0682		.0739	.0543	.0681	.1070	.0493
1,500	.0905	.0900		.0956	.0729	.0890	.1322	.0672
2,000	.1087	.1081		.1136	.0885	.1062	.1517	.0819
2,500	.1241	.1236	.1752	.1291	.1022	.1211	.1680	.0939
3,000	.1375	.1368		.1427	.1141	.1342	.1820	.1040
3,500	.1494	.1484		.1547	.1247	.1457	.1945	.1127
4,000	.1601	.1588		.1654	.1344	.1558		.1200
4,500	.1698	.1682		.1750	.1434	.1649	$_g$	.1261
5,000	.1787	.1767$_b$	.2059	.1838	.1517$_e$	.1731	.2475	.1312
10,000	.2393$_a$	.2834	.2479	.2413	.2303$_e$	.2304	.2914	
15,000	.3152^a	.3090	.2759	.2781	.2574	.2828^f	.3134	
20,000	.3388	.3287	.2969	.3032	.2776	.3030	.3293	
25,000	.3563	.3439	.3163	.3221	.2937	.3202	.3416	
30,000	.3702	.3571	.3273	.3371	.3066	.3352	.3511	
35,000	.3811	.3690	.3386	.3501	.3173	.3484	.3589	
40,000	.3898	.3798	.3481	.3621	.3264	.3602	.3653	

a Freezes at 12,440. $\Delta V/V_0$ .2586 and .2987
b Freezes at 5,500. $\Delta V/V_0$ .1850 and .2524
c Freezes at 650. $\Delta V/V_0$ .0333 and .1300
d Liquid throughout
e Freezes at 7,500. $\Delta V/V_0$ .1828 and .2121
f Freezes at 11,140. $\Delta V/V_0$ .2241 and .2451
g Freezes at 4,400. $\Delta V/V_0$ .2139 and .2391

Of the substances in Table II, special comment in addition to that already made in the discussion of previous measurement, is required for methylcyclohexane.   In addition to the figures in the table which pertain to the liquid phase, an isolated point was obtained for the solid phase at 12,440 kg/cm^2.   At this pressure, $\Delta V/V_0$ for the solid was 0.2707 and for the liquid 0.2506.   Methylcyclohexane is one of the rare substances, of which only one example has been found before,[20] which do not experience a change of phase on the initial application of pressures in excess of the pressure of thermodynamic equilibrium. If pressure is maintained for a considerable time far beyond the equilibrium pressure, some process of nucleus formation slowly occurs in the liquid, so that when pressure is released to a point sufficiently close to the equilibrium pressure, solidification occurs with a paradoxical decrease of volume.

In Table III are collected the results for the eight miscellaneous organic compounds.   The general character of the numerical results is the same as that in Tables I and II.   In other words, introducing other atoms beside hydrogen and carbon into the molecule has not produced any spectacular changes in the compressions.   The abnormally high initial compressibility of the light fluorocarbon is to be no-

TABLE IV

COMPRESSION OF DI-METHYL SILOXANE POLYMERS

Pressure kg/cm^2	$\Delta V/V_0$						
	Dimer	Trimer	Tetramer	Pentamer	Hexamer	Heptamer	Octamer
0	.0000	.0000[b]	.0000[b]	.0000[b]	.0000[b]	.0000[b]	.0000[b]
500	.0586	.0568	.0531	.0532	.0485	.0496	.0456
1,000	.0960	.0921	.0864	.0862	.0800	.0818	.0780
1,500	.1227	.1174	.1110	.1102	.1039	.1055	.1012
2,000	.1434	.1373	.1308	.1291	.1231	.1245	.1200
2,500	.1603	.1539	.1470	.1450	.1393	.1403	.1357
3,000	.1752	.1679	.1609	.1587	.1530	.1539	.1492
3,500	.1882[a]	.1800	.1730	.1707	.1647	.1659	.1611
4,000		.1908	.1838	.1813	.1751	.1766	.1719
4,500		.2007	.1936	.1909	.1847	.1862	.1813
5,000	.2518	.2099	.2026	.1996	.1937	.1947	.1898
10,000	.2928	.2736	.2590	.2559	.2498	.2514	.2486
15,000	.3184	.3096	.2933	.2895	.2865	.2831	.2790
20,000	.3384	.3332	.3149	.3113	.3052	.3051	.3000
25,000	.3546	.3508	.3310	.3272	.3212	.3215	.3163
30,000	.3679	.3650	.3442	.3403	.3347	.3350	.3298
35,000	.3797	.3774	.3555	.3525	.3470	.3467	.3414
40,000	.3905	.3886	.3660	.3637	.3583	.3570	.3515

a Freezes at 3,790. $\Delta V/V_0$ .1952 and .2315
b Liquid throughout

ticed, the largest of any measured here. At 40,000, however, the volume compression of methylene chloride has overtaken it; the obvious reason is its larger change of volume on freezing.

In Table IV are given the compressions of the di-methyl siloxane polymers, and in Table V the similar Dow Corning fluids. The

TABLE V
COMPRESSION OF "DOW-CORNING FLUIDS"

Pressure kg/cm²	$\Delta V/V_0$								
	500–0.65	500–1.00	500–2.00	500–12.8	200–100	200–350	200–1,000	200–12,500	550–112
0	.0000	.0000[b]	.0000[b]	.0000[b]	.0000[b]	.0000[b]	.0000[b]	.0000[b]	.0000[b]
500	.0634	.0536	.0485	.0447	.0449	.0447	.0458	.0446	.0305
1,000	.1004	.0884	.0821	.0729	.0734	.0742	.0736	.0729	.0512
1,500	.1259	.1139	.1069	.0949	.0946	.0955	.0947	.0933	.0675
2,000	.1462	.1341	.1267	.1131	.1120	.1128	.1123	.1104	.0813
2,500	.1633	.1508	.1434	.1285	.1271	.1278	.1274	.1253	.0934
3,000	.1782	.1651	.1579	.1416	.1402	.1411	.1403	.1384	.1043
3,500	.1916	.1776	.1705	.1531	.1519	.1526	.1517	.1500	.1143
4,000	a	.1884	.1817	.1633	.1620	.1627	.1618	.1602	.1235
4,500		.1979	.1917	.1726	.1711	.1716	.1705	.1690	.1320
5,000	.2571	.2066	.2007	.1813	.1793	.1796	.1787	.1771	.1399
10,000	.2970	.2633	.2604	.2367	.2349	.2374	.2324	.2304	.1785
15,000	.3244	.2960	.2949	.2689	.2652	.2676	.2615	.2594	.2083
20,000	.3442	.3170	.3151	.2906	.2863	.2888	.2820	.2808	.2305
25,000	.3594	.3328	.3308	.3076	.3032	.3056	.2990	.2980	.2480
30,000	.3720	.3457	.3456	.3214	.3173	.3294	.3131	.3125	.2632
35,000	.3827	.3566	.3577	.3329	.3294	.3410	.3249	.3246	.2765
40,000	.3921	.3658	.3689	.3429	.3404	.3519	.3349	.3350	.2889

a Freezes at 4,010. $\Delta V/V_0$ .2044 and .2404
b Liquid throughout

polymers, through the octamer, fall within the range of the other liquids measured in this paper, but are among the more compressible of them. The compression in general diminishes with increasing molecular weight. The curve of compression against molecular weight is, however, not smooth but alternates, the compression of the odd polymers being above a smooth curve through the even members. This is evident from a glance at the row of compressions for 500 kg/cm² or for 40,000. The amplitude of oscillation from even to odd is less at the higher pressures, as might be expected.

The only pure liquid brought to freeze by pressure is the dimer. This is distinctly not what might be expected, but the higher members of the series would be expected to have progressively lower freezing pressures, as for example, in the series of normal paraffins. The reason for the failure of the higher members to freeze under pressure

should be investigated further. It may possibly be connected with inadequate chemical purity, but it seems more likely that it is connected with the abnormally rapid increase of viscosity of these liquids under pressure, an effect which would facilitate subcooling because of the difficulty of nucleus formation.

The Dow Corning fluids show the same progression that would be expected from the pure polymers, carried somewhat further, since the more viscous members of the series contain polymers much higher than the octamer. The same failure to freeze under pressure except for the first member of the series, is shown here as was shown by the pure polymers. With indefinitely great increase of viscosity, that is, with indefinite increase of length of the polymeric chain, the compression appears to approach an asymptotic value. This again is what might be expected. It is obvious that the mechanism responsible for viscosity must be entirely different from that responsible for compression.

The single example of a Dow Corning fluid of the 550 series is distinctly less compressible than the others, corresponding to its radically different structure.

Finally, if the results of this paper be compared with the results for the organic compounds in a previous paper over the same pressure range,[1] a general parallelism will be found. In the former paper there are, however, a considerable number of examples of smaller compressions. The organic compounds of this paper, especially the hydrocarbons, do not include examples of as close binding as frequently occur in organic compounds.

LYMAN LABORATORY OF PHYSICS,
Harvard University, Cambridge, Mass.

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